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**SPRAYING MATERIAL AND SPRAYING FABRICATION METHOD WHICH  
USES THAT**

[吹付材料及びそれを用いた吹付工法]

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USES THAT**

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(57) [Abstract]

[Problems to be Solved by the Invention]

Offer of spraying material and spraying fabrication method to which flow property is large,  
is superior in strength manifestation, powder dust decrease, and rebound decrease.

[Means to Solve the Problems]

Spraying material, which contains powder polycarboxylic acid high performance de-  
watering agent which consists of calcium salt of copolymer of polyalkylene glycol mono  
alkenyl ether and maleic acid which are shown with cement and Chemical Formula (1)

a = 0 is desirable in Chemical Formula (1).

[Chemical Formula 4]

Translator's Notes: [Chemical Formula 4]  
(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

Spraying material, quick setting agent, coagulation promotion medicine, and coagulation lag medicine which designate calcium aluminate as main component, may contain mulling agent such as powder dust decreasing agent, ultra fine powder, and fiber.

[Claim(s)]

[Claim 1]

Containing powder polycarboxylic acid high performance de-watering agent which consists of calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with cement and Chemical Formula (1) spraying material, which becomes and makes feature

[Chemical Formula 1]

Translator's Notes: [Chemical Formula 1]  
(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

[Claim 2]

Containing powder polycarboxylic acid high performance de-watering agent, and calcium aluminate which consist of calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with cement, Chemical Formula (1) containing quick setting agent which becomes, spraying material, which is stated in Claim 1 or 2 which becomes and makes feature

[Claim 3]

It is a  $a=0$  in Chemical Formula (1) and spraying material, which is stated in the Claim 1 or 2 which is made feature

[Claim 4]

Furthermore, quick setting agent containing coagulation promotion medicine, spraying material, which is stated in Claim 1~3 which becomes and makes feature

[Claim 5]

Furthermore, coagulation lag medicine, containing mulling agent of one, two or more kinds which is chosen from powder dust decreasing agent, ultra fine powder, and group which consists of fiber spraying material, which is stated in Claim 1~4 which becomes and makes feature

[Claim 6]

Using spraying material which is stated in Claim 1~5, spraying fabrication method, which becomes and makes feature

[Description of the Invention]

[0001]

[Technological Field of Invention]

this invention contains specific powder polycarboxylic acid high performance de-watering agent, blowing regards the spraying material and spraying fabrication method which uses that to ground aspect which is exposed in road, railroad, and derived water line or other tunnel.

Furthermore, with this invention, generic doing dry cement mortar, cement mortar, paste, and concrete, you call cement mortar or concrete.

[0002]

[Prior Art]

Until recently, tunnel excavation, etc., spraying fabrication method of quick setting characteristic concrete which combines quick setting agent to the concrete in order to prevent fall of ground which is exposed is done, (Japan Examined Patent Publication Sho 52-4149 disclosure).

Usually, it installed this fabrication method, in excavation construction site, it makes spraying concrete with weighing mixed plant of cement aggregate and water, conveys that by agitator car, pneumatic transport does with concrete pump, with confluence tube, which is provided on middle, it mixes with quick setting agent which pneumatic transport is done from other, Until on ground aspect it becomes predetermined thickness, as quick setting characteristic spraying concrete blowing it is a fabrication method.



With this fabrication method in order to give flow property to spraying concrete, when manufacturing spraying concrete, adds high performance de-watering agent which possesses de-watering property, air permeability, and the ability to disperse is.

As high performance de-watering agent, you can list naphthalene sulfonate system, melamine sulfonate system, and polycarboxylic acid system etc.

Mixing to various cement filler as powder, you can use high performance de-watering agent of naphthalene sulfonate type and melamine sulfonate type, for spraying material.

But, high performance de-watering agent of naphthalene sulfonate type, when it jointly uses with powder dust decreasing agent and rebound preventing agent of cellulose type, had deficiency that de-watering property, air permeability, and the ability to disperse disappears.

Deficiency that there was a high performance de-watering agent of naphthalene sulfonate type and melamine sulfonate type the improved effect of intensity is small together.

Furthermore, spraying concrete which is manufactured is kneaded and when it leaves, change over time of slump is large, kneads spraying concrete with the mechanical/ electrical trouble, etc., of blowing apparatus and when necessity to leave occurs, the concrete becomes hard, causes adverse effect to pneumatic transport behavior, becomes difficult, to mix to quick setting agent and uniform becomes non-uniform quick setting characteristic spraying concrete in qualitative. There was a deficiency that or other hazard where concrete falls from tunnel surface occurs.

[0003]

Then, it reached point where polycarboxylic acid high performance de-watering agent where slump loss is small is used.

flow property of spraying concrete and method which improves quick setting characteristic are proposed as polycarboxylic acid high performance de-watering agent, polyalkylene glycol mono allyl ether-maleic acid copolymer, polyalkylene glycol mono (meth) acrylic acid ester- (meth) acrylic acid copolymer, water soluble olefin and  $\alpha$  and  $\beta$ -unsaturated by using saponate, of copolymer, sulfonation styrene-maleic acid copolymer of di-carboxylic acid derivative and saponate etc of the styrene-maleic acid copolymer, etc., (Japan Examined Patent Publication Hei 5-53743 disclosure, Japan Unexamined Patent Publication Hei 3-153550 disclosure ).

[0004]

[Problems to be Solved by the Invention]

But, these polycarboxylic acid high performance de-watering agent were not something which still is satisfied in point of water reduction ratio, slump loss, and strength

manifestation.

As for de-watering agent in order without adding not to have with spraying site, it is a powder which premix can be made various powder body material beforehand, it is desirable, but conventional polyalkylene glycol (meth) acrylic acid ester- (meth) acrylic acid copolymer, usually unless in wax state and malt syrup condition, it is a aqueous solution with room temperature, had problem that cannot be used.

Because of that, cement, quick setting agent or other powder cement mulling agent, and fly ash or other powder cement filler and the de-watering agent with site weighing/ must be added specially separately in spraying job, there was a problem that workability decreases considerably.

Then, ability to disperse, quick setting characteristic, it reached point where it can seek spraying material which it can be satisfied from point of the intensity, and workability.

[0005]

As for this inventor, as for result which these problem various was examined, by using specific powder polycarboxylic acid high performance de-watering agent which premix can be made portland cement, alumina cement, and mulled cement or other various cement, silica fume, furnace slag, and fly ash or other various cement filler, and other powder high performance de-watering agent, powder dust decreasing agent, powder foam inhibitor, coagulation promotion medicines, and coagulation lag medicine or other various powder cement mulling agent or other various powder body material beforehand, slump retention, quick setting characteristic, Obtaining knowledge where strength manifestation characteristic, powder dust low degradation, rebound characteristic of initial stage/long period, and high quality spraying material which is superior in workability are acquired, this invention it reached to completion.

[0006]

[Means to Solve the Problems]

Namely it is a spraying material where this invention becomes and containing powder polycarboxylic acid high performance de-watering agent which consists of calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and the maleic acid which are shown with cement and Chemical Formula (1) makes feature.

[Chemical Formula 2]

Translator's Notes: [Chemical Formula 2]  
(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

And, containing powder polycarboxylic acid high performance de-watering agent, and calcium aluminate which consist of the calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with the cement, Chemical Formula (1) containing quick setting agent which becomes, with the spraying material which is stated in Claim 1 or 2 which becomes and makes feature, it is a  $a=0$  in Chemical Formula (1) and with said spraying material which is made feature, furthermore, Quick setting agent containing coagulation promotion medicine, with said spraying material which becomes and makes feature, furthermore, coagulation lag medicine, containing mulling agent of one, two or more kinds which is chosen from the powder dust decreasing agent, ultra fine powder,, and group which consists of fiber with said spraying material which becomes and makes feature, using said spraying material, it is a spraying fabrication method which becomes and makes feature.

[0007]

[Embodiment of the Invention]

Below, this invention is explained in detail.

[0008]

Usually it is marketed as cement which is used with this invention, normally, quickly you can list various mulled cement, and commercial fine particle cement, etc., which mix fly ash and furnace slag, etc., to these portland cement of strong, midrange heating, and super quickly strong or other various portland cement, to fine powder convert various portland cement and various mulled cement and are possible to use.

[0009]

Powder polycarboxylic acid high performance de-watering agent which is used with this invention is calcium salt of copolymer of polyalkylene glycol alkenyl ether and maleic acid which are shown with below-mentioned Chemical Formula (1), (You call main copolymer calcium salt below).

[Chemical Formula 3]

Translator's Notes: [Chemical Formula 3]  
(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

[0010]

In the aforementioned Chemical Formula (1), in A ethylene group of carbon number 2 is desirable in point where water solubility of this copolymer calcium salt is large.

As for alkyl group which is shown with R production of copolymer being easy, methyl group is desirable in point where water solubility is large.

n 1 - 60 is desirable in point of ability to disperse.

When it is under 1, ability to disperse is not acquired, when, it exceeds 60, viscosity of reaction mixture becomes large at time of copolymer production, there is a possibility reactivity becoming small.

[0011]

Weight average molecular weight of this copolymer calcium salt 3000 - 100000 is desirable.

When it is under 3000, ability to disperse to decrease, exceed 100000 and not be able to expect further effect, there is a possibility of becoming the high cost.

Weight average molecular weight designated for example known polyethylene glycol as standard substance, used those which were measured due to aqueous system GPC.

[0012]

It can produce copolymer (You call main copolymer below) of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with Chemical Formula (1) with manufacturing method of public knowledge.

With method which is stated in for example Japan Unexamined Patent Publication Showa 64- 109 disclosure and Japan Unexamined Patent Publication Hei 8-46652 disclosure, in the organic solvent and under condition of without any solvents, radical polymerization doing copolymer and polyalkylene glycol mono vinyl ether of polyalkylene glycol mono allyl ether and maleic anhydride and copolymer of maleic anhydride, with radical initiator, it can produce.

In polyalkylene glycol mono alkenyl ether which is used for this copolymer, it is superior in copolymeriz-ability, productivity, and de-watering property of maleic anhydride, polymerization rate is quick, and, in point which can remove not reacted impurity in copolymer which is acquired easily, the polyalkylene glycol mono vinyl ether which is a  $\alpha=0$  in Chemical Formula (1) is desirable.

Furthermore, as for copolymerization mole ratio of polyalkylene glycol alkenyl ether and the maleic anhydride, in point where copolymer is acquired easily,  $\frac{1}{2} - 2/1$  is desirable,  $1/1.2 - 1.2/1$  is more desirable.

It is possible to use citraconic acid anhydride and maleimide in place of also, maleic anhydride, but maleic anhydride is desirable in point of ability to disperse and cost.

[0013]

This copolymer calcium salt is acquired this copolymer and calcium salt compound by reacting.

As manufacturing method, in solution which organic solvent solution and copolymer of copolymer heating and melting is done, adding slurry which mixes calcium hydroxide and the calcium hydroxide and water, neutralization reaction after doing, drying/ powder fragment the method of doing. organic solvent of copolymer stripping doing with heated steam, you can list method etc which after recovering, reacting with calcium hydroxide, the drying/ powder fragment does copolymer aqueous solution.

[0014]

average particle diameter of powder polycarboxylic acid high performance de-watering agent which consists of this copolymer calcium salt especially is not limited.  $0.1 - 200 \mu m$  are desirable.

0.1 When it is under the  $\mu m$ , cost which making fine particles is done to become high, when it exceeds  $200 \mu m$ , powder polycarboxylic acid high performance de-watering agent without melting rapidly, various powder body material and segregation doing the occasion where dry blend it does there is a possibility effect not being acquired.

fine powdering is done powder polycarboxylic acid high performance de-watering agent as method which usually, you can list powder mist drying, powder fragment, and solvent precipitation etc.

[0015]

As for amount used of powder polycarboxylic acid high performance de-watering agent

which consists of main copolymer calcium salt of Chemical Formula (1) 0.01 - 5.0 parts by weight are desirable in relation to cement 100 parts by weight, 0.02- 5.0 parts by weight are more desirable.

0.01 When under part by weight satisfactory dispersing performance is not acquired, exceeds 5.0 parts by weight there is a possibility of causing coagulation lag and material separation.

[0016]

Because it is a polycarboxylic acid high performance de-watering agent of powder, you can use main copolymer calcium salt of Chemical Formula (1) as various cement, various cement filler, and premix product which is mixed with various powder cement mulling agent beforehand.

Effect of powder dust decrease and rebound prevention can be granted by mixing to quick setting agent which consists of for example calcium aluminate and the alkali metal aluminate and alkali metal carbonate salt or other coagulation promotion medicine beforehand.

[0017]

With this invention, in point which causes coagulation of cement mortar or concrete in initial stage, uses calcium aluminate as quick setting agent is desirable.

calcium aluminate calls quick setting component which causes coagulation of the concrete in initial stage, powder fragment are done those etc which can list the calcium aluminate heat treated substance which when  $C_{12}A_7$  is designated as A, is shown the CaO with  $C_3A$ ,  $C_{12}A_7$ , CA, and  $CA_2$  etc as mineral component.

Furthermore,  $C_{11}A_7/CaX_2$  which replaces CaO of one of the aluminosilicate,  $C_{12}A_7$  which contains  $SiO_2$  as other mineral component, with  $CaF_2$  or other halide (As for X fluorine or other halogen),  $C_4A_3/SO_3$ , alumina cement, and sodium, potassium, and part solid solution is done calcium aluminate etc which include  $SO_3$  component you can list lithium or other alkali metal, can use crystalline and amorphous in each case.

Among these, in point of reactivity, amorphous calcium aluminate which heat treated substance which corresponds to  $C_{12}A_7$  composition quench is done is desirable.

As for granularity of calcium aluminate, in quick setting characteristic and the initial stage strength manifestation characteristic point,  $3000\text{ cm}^2/\text{g}$  or more are desirable at brain value,  $4000\text{ cm}^2/\text{g}$  or more are more desirable.

When it is under  $3000\text{ cm}^2/\text{g}$ , there is a possibility quick setting characteristic and initial stage strength manifestation characteristic decreasing.

[0018]

As for amount used of calcium aluminate, 1 - 20 parts by weight are desirable in relation to cement 100 parts by weight, 5 - 15 parts by weight are more desirable.

When under 1 part by weight initial stage coagulation does not happen, exceeds 20 parts by weight there is a possibility of obstructing long period strength manifestation characteristic.

[0019]

With this invention, promoting coagulation of cement, in point which gives quick setting power to cement mortar, uses coagulation promotion medicine is desirable.

[0020]

As coagulation promotion medicine, sodium aluminate, potassium aluminate, and aluminic acid lithium or other alkali metal aluminate, sodium carbonate, potassium carbonate, and lithium carbonate or other alkali metal carbonate salt, you can list sodium hydroxide, potassium hydroxide, and lithium hydroxide or other alkali metal hydroxide, sodium sulfate, potassium sulfate, aluminum sulfate, and alum or other sulfate, hydrated lime, and amine compound, etc are possible to jointly use these one, two or more kinds.

Among these in coagulation characteristic point, use of alkali metal aluminate and alkali metal carbonate salt is desirable.

With this invention, in point of improvement of initial stage coagulation characteristic and strength manifestation characteristic, calcium aluminate and coagulation promotion medicine are jointly used are desirable.

Furthermore, when depending, melting in water, it is possible to use coagulation promotion medicine as liquid.

[0021]

As for amount used of coagulation promotion medicine, when calcium aluminate is not jointly used, 1 - 20 parts by weight are desirable in relation to cement 100 parts by weight, 5 - 15 parts by weight are more desirable.

When under 1 part by weight coagulation of cement mortar does not promote, exceeds 20 parts by weight there is a possibility of causing adverse effect to long period strength manifestation characteristic.

[0022]

When also, calcium aluminate is jointly used, as for amount used of coagulation promotion medicine, 0.5 - 50 parts by weight are desirable in relation to calcium aluminate 100 parts by weight, 1 - 30 parts by weight are more desirable.

0.5 When under parts by weight coagulation of cement mortar does not promote, exceeds 50 parts by weight there is a possibility of causing adverse effect to long period strength manifestation characteristic.

[0023]

As for amount used of quick setting agent when calcium aluminate and the coagulation promotion medicine are mixed, 1 - 20 parts by weight are desirable in relation to the cement 100 parts by weight, 5 - 15 parts by weight are more desirable.

When under 1 part by weight coagulation of cement mortar does not promote, exceeds 20 parts by weight there is a possibility of obstructing long period strength manifestation.

[0024]

With this invention, furthermore, coagulation lag medicine, uses mulling agent of the one, two or more kinds which is chosen from ultra fine powder, powder dust decreasing agent and group which consists of fiber is desirable.

[0025]

coagulation lag medicine has influence which setting time of cement mortar the delay is done, organic acid, alkali metal carbonate salt, can list alcohols, phosphate, and borate etc.

[0026]

As organic acid, you can list gluconic acid, tartaric acid, citric acid, malic acid, and lactic acid or these salt etc.

As for amount used of organic acid, 0.05 - 3 parts by weight are desirable in relation to cement 100 parts by weight, 0.1 - 2 parts by weight are more desirable.

0.05 When under parts by weight there is not an effect, exceeds 3 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.



[0027]

As alkali metal carbonate salt, you can list sodium carbonate, potassium carbonate, sodium bicarbonate, and potassium hydrogen carbonate etc.

As for amount used of alkali metal carbonate salt, 0.1 - 10 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 5 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 10 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0028]

As alcohols, propylene oxide and water soluble polymer polyols etc which is a adduct which the ethylene oxide addition polymerization is done can list low molecular weight water soluble alcohol and to polyethylene glycol or polypropylene glycol or other polyalkylene glycols and the triethanolamine or other amino alcohols which one or greater it possesses ethanol, methanol, ethyleneglycol, and glycerine or other hydroxy group.

As for amount used of alcohols 0.1 - 5 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 3 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 5 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0029]

As phosphate, you can list monosodium phosphate, disodium phosphate, trisodium phosphate, sodium hexametaphosphate, sodium tripolyphosphate, and tri sodium metaphosphate etc.

It is possible to use potassium in place of also, sodium.

Among these, in point which is difficult to obstruct long period strength manifestation characteristic, sodium tripolyphosphate is desirable.

As for amount used of phosphate, 0.1 - 5 parts by weight are desirable in relation to cement 100 parts by weight, 0.2 - 2 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 5 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0030]

As borate, you can list sodium borate and potassium borate etc.

As for amount used of borate 0.1 - 10 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 5 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 10 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0031]

In these coagulation lag medicines in point of initial stage strength manifestation, combined use of organic acid and alkali carbonate is desirable.

[0032]

When organic acid and alkali carbonate are jointly used, as for amount used of the alkali carbonate, 10 - 1000 parts by weight are desirable in relation to organic acid 100 parts by weight, 50 - 700 parts by weight are more desirable.

When under 10 parts by weight there is not an effect, exceeds 1000 parts by weight there is a possibility delayed decreasing.

As for amount used of blend of organic acid and alkali carbonate, 0.1 - 10 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 5 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 10 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0033]

Powder dust decreasing agent which is used with this invention has powder dust low degradation and influence which possesses rebound prevention property, methyl cellulose, hydroxypropyl cellulose, ethyl cellulose, methylethyl cellulose, you can list polyvinyl alcohol, polyacrylic acid, polyvinyl acetate, and polyethylene-polyvinyl acetate copolymer etc.

Among these, in point whose effect is large, methyl cellulose is desirable.

As for amount used of powder dust decreasing agent, 0.001 - 1.0 parts by weight are

desirable in relation to cement 100 parts by weight, 0.01 - 0.5 parts by weight are more desirable.

0.001 When under part by weight there is not an effect, exceeds 1.0 parts by weight there is a possibility viscosity becoming large, causing hindrance to pneumatic transport behavior.

[0034]

ultra fine powder which is used with this invention has influence of average particle diameter 10  $\mu$  m or less, decrease of amount of cement and powder amount of dust and improvement of pneumatic transport behavior of concrete are made possible.

As ultra fine powder, fine powder slag, fly ash, bentonite (DANA 71.3.1a.1-2 ), you can list kaolin, and silica fume etc.

Among these in point whose effect is large, silica fume is desirable.

As for amount used of ultra fine powder, 1 - 100 parts by weight are desirable in relation to cement 100 parts by weight, 2 - 30 parts by weight are more desirable.

When under 1 part by weight there is not an effect, exceeds 100 parts by weight there is a possibility coagulation and hardening being late.

[0035]

fiber which is used with this invention be able to use inorganic and organic in each case, impact resistance and elasticity of spraying concrete it is something which improves.

As for length of fibrous substance, in point of pneumatic transport behavior and the compatibility, 50 mm or less are desirable, 30 mm or less is more desirable.

When it exceeds 50 mm, there is a possibility spraying concrete being plugged in pneumatic transport.

As fiber of inorganic, you can list glass fiber, carbon fiber, rock wool, asbestos, ceramic fiber, and metal fiber, etc you can list vinylon fiber, polyethylene fiber, polypropylene fiber, poly acrylic fiber, cellulose fiber, polyvinyl alcohol fiber, polyamide fiber, pulp, linen, wooden wool, and wood chip etc as fiber of organic.

Among these, vinylon fiber and metal fiber are desirable in point of the economy.

As for amount used of fiber, 0.5 - 7 parts by weight are desirable in relation to cement 100

parts by weight, 1 - 5 parts by weight are more desirable.

0.5 When under parts by weight there is not an effect, exceeds 7 parts by weight there is a possibility flow property of spraying concrete decreasing.

[0036]

As for amount used of water with this invention, 35 - 60 parts by weight or less are desirable in relation to cement 100 parts by weight, 40 - 55 parts by weight are more desirable.

When it is under 35 parts by weight, not be able to mix with mixer, when it exceeds 60 parts by weight, there is a possibility strength manifestation characteristic becoming bad.

[0037]

As for coarse aggregate and fine aggregate or other aggregate which are used with this invention moisture absorption being low, those where aggregate intensity is high are desirable, but it is not something which especially is restricted.

Those of maximum diameter 20 mm or less are desirable as coarse aggregate, when pumping behavior is considered, those of maximum diameter 5~15 mm are more desirable.

Those of maximum diameter 5 mm or less are desirable as fine aggregate, can list river sand, pit sand, lime sand, and silica sand etc.

[0038]

When using spraying material of this invention, it is possible to use foam inhibitor in order to adjust taking amount of air.

As foam inhibitor, lower alcohols, higher alcohol, oils, fatty acids, fatty acid esters, phosphate ester, metal soap, mineral oil, silicones, and polymer etc of polyethers are listed.

Among these polymer is desirable in point whose effect is large.

As polymer, portion of end group of polyoxyethylene polypropylene adduct or other polyoxy alkylene and polyoxy alkylene with the alkyl group etherification portion of end group of polyoxy alkylene alkyl ethers, polyoxy alkylene which are done with aryl group and alkyl aryl group etherification polyoxy alkylene (alkyl) aryl ether sulfuric acid ester salt which portion of end group of polyoxy alkylene fatty acid esters, polyoxy alkylene which portion of end group of polyoxy alkylene (alkyl) aryl ethers, polyoxy alkylene which are done fatty acid esterification are done sulfuric acid esterification are done, And amination

are done polyoxy alkylene alkyl amines or other polyoxy alkylene etc which can list portion of the end group of polyoxy alkylene.

As method of use of foam inhibitor, method of adding beforehand in the middle which produces this copolymer calcium salt. Impregnating foam inhibitor in white carbon, and silica or other inorganic powder body the method of making powder foam inhibitor. And you can list this copolymer calcium salt and with various powder body material the method etc which premix is done.

[0039]

As for amount used of foam inhibitor, 0.01 - 10 parts by weight are desirable in relation to powder polycarboxylic acid high performance de-watering agent 100 parts by weight which consists of this copolymer calcium salt, 0.05 - 5 parts by weight are more desirable.

0.01 When it is under part by weight, there not to be a de-foaming effect, exceed 10 parts by weight and not be able to expect improvement of de-foaming effect, there is a possibility taking amount of air rather becoming many.

[0040]

With spraying fabrication method of this invention, you work spraying from property, economy, and the ability to fabricate, etc., which are required, as dry cement mortar, cement and contain water the cement mortar, paste, and concrete which contain cement, it is possible, while flowing confluent mixing it is possible to do quick setting agent which contains calcium aluminate in according to need, these.

[0041]

As spraying fabrication method, you can list dry type spraying method and wet type spraying method.

As dry type spraying method, although dry cement mortar which mixes cement and the aggregate is manufactured, also according to need quick setting agent carries mixes with belt conveyor, pneumatic transport does, supplies quick setting agent, water to order midway and blowing can list method etc.

As wet type spraying method, it manufactures cement mortar which mixes cement, aggregate, and water pneumatic transport it does according to need quick setting agent from one side of Y letter tube which is provided on the for example middle can list cement mortar and confluent mixing does and blowing method etc.

In case of these spraying fabrication method, powder polycarboxylic acid high performance de-watering agent, coagulation promotion medicine and coagulation lag medicine which consist of this copolymer calcium salt, be able to mix mulling agent and the filler other than

quick setting agent such as powder dust decreasing agent, ultra fine powder, and fiber, on both side of mortar side and quick setting agent side, pneumatic transport is good doing in only one side, to jointly use to both sides is possible.

If it can blow spraying material which consists of finally this invention there is not a problem.

coagulation promotion medicine, in point where effect which is superior is acquired, uses powder dust decreasing agent, ultra fine powder, and fiber, to mortar side is desirable.

Furthermore, when depending, it mixes quick setting agent and the water, it is possible to use as quick setting agent slurry.

[0042]

Regarding spraying fabrication method of this invention, you can use spraying facility, etc., of past use.

As for usually, as for spraying pressure 2 - 5 kg/cm<sup>2</sup>, spraying velocity they are 4 - 20 m<sup>3</sup>/h.

If spraying facility spraying is done in fully, it is not something which especially is limited, ants bar corporation trade name "ants bar 280" etc., you can use quick setting agent pneumatic conveyor equipment "Natom Crete," etc., to pneumatic transport of quick setting agent in pneumatic transport of for example concrete.

[0043]

[Working Example(s)]

this invention is explained in detail below, on basis of Working Example.

[0044]

(Working Example 1)

It designated unit amount of each material as cement 360 kg/m<sup>3</sup>, coarse aggregate 734 kg/m<sup>3</sup>, fine aggregate 1089 kg/m<sup>3</sup>, and water 191 kg/m<sup>3</sup>, mixing high performance de-watering agent of quantity which is shown in Table 1, in relation to cement 100 parts by weight it made spraying concrete.

Concerning this spraying concrete, slump and compressive strength were measured.

However, n of main copolymer calcium salt in used material is n in the Chemical Formula (1).

Result is shown in Table 1.

[0045]

(used material )

cement: marketing normally portland cement density 3.16

coarse aggregate: Toyama Prefecture Sakaigawa product gravel, chart dry state, maximum size 15 mm or less, density 2.64

fine aggregate: Toyama Prefecture Sakaigawa product river sand, chart dry state, maximum size 5 mm or less, density 2.61

Water: tap water, 20 deg C

Main copolymer calcium salt, methoxy polyethylene glycol vinyl ether-maleic acid copolymer calcium salt, n=45, weight average molecular weight 20000, powder body of high performance de-watering agent 1:, particle diameter 200  $\mu$  m or less

Main copolymer calcium salt, methoxy polyethylene glycol vinyl ether-maleic acid copolymer calcium salt, n=10, weight average molecular weight 20000, powder body of high performance de-watering agent 2:, particle diameter 200  $\mu$  m or less

Main copolymer calcium salt, methoxy polyethylene glycol allyl ether-maleic acid copolymer calcium salt, n=10, weight average molecular weight 20000, powder body of high performance de-watering agent 3:, particle diameter 200  $\mu$  m or less

high performance de-watering agent 4: commercial naphthalene sulfonate high performance de-watering agent, powder body

high performance de-watering agent 5: commercial melamine high performance de-watering agent, powder body high performance de-watering agent 6: commercial methoxy polyethylene glycol methacrylic acid ester

-methacrylic acid copolymer salt high performance de-watering agent, aqueous solution which is made main component

high performance de-watering agent 7: styrene-maleic acid copolymer salt, weight average proportion 40000, powder body, particle diameter 200  $\mu$  m or less

[0046]

(measurement method )

ス	ラ	ブ:J		S	A			0		According to	て Measurement.
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Pouring in Lee jp7, it formed, after hardening mold removal did, the curing in water did with 20 deg C, measured with 20 t pressure resistance test machines.

It measured due to weight average molecular weight: aqueous system GPC.

weight average molecular weight designated known polyethylene glycol as standard substance.



[0047]  
[Table 1]

Table 1

Exprimment	High Quality De-watering agent	Slump			Compression Strength		Notes
		Right After	30 Minutes	60 Minutes	7 Days	28 Days	
							Compression Example
							Carried Out Example [Translator's Note: 12 Entries]
							ComparisonExaple [Translator'sNote: Last For Entries]

[Underneath Table 1]

Parts by weight of the high quality dewatering agent is against 100 parts by weight of cemnt.  
(However, high quality dewatering agent (30 Minutes) is a converted amount for the solid part). " - "  
Water compression strenght was impossible to extract because of lack of pressure.

[0048]

(Working Example 2 )

Mixing coagulation promotion medicine of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10. 3 parts by weight, and Table 2, it executed other than thing which it makes the spraying concrete, in same way as Working Example 1.

Result is shown in Table 2.

(used material )

coagulation promotion medicine A: marketing sodium aluminate

coagulation promotion medicine B: marketing sodium carbonate

Coagulation promotion medicine C: marketing alum

[0049]  
[Table 2]

Table 2

Experiment	Coagulation watering agent	Compression Strength		Notes	
					Carried Out Example [Translator's Note: 16 Entries]

[Underneath Table 2]

h is hours, d is days, parts by weight of the coagulation promotion agent is against 100 parts by weight of cement. " - " under compression strength was impossible to extract because of lack of pressure.

[0050]

(Working Example 3 )

It designated unit amount of each material as cement 360 kg/m<sup>3</sup>, coarse aggregate 734 kg/m<sup>3</sup>, fine aggregate 1089 kg/m<sup>3</sup>, and water 191 kg/m<sup>3</sup>, mixing high performance de-watering agent 1 of quantity which is shown in Table 3, in relation to cement 100 parts by weight it made spraying concrete, pneumatic transport it did this making use of concrete pneumatic transport machine "ants bar 280".

From one side of Y letter tube which is provided midway, 10 parts by weight mixing in relation to cement 100 parts by weight, pneumatic transport it did quick setting agent which consists of calcium aluminate, with quick setting agent addition machine "Denkanatom Creet," confluent mixing did and manufactured quick setting characteristic spraying concrete.

This quick setting characteristic spraying concrete with spraying velocity of 4 m<sup>3</sup>/h blowing was done in simulation tunnel of 30 min height 3.5m, width 2.5m, powder amount of dust and rebound ratio were measured.

Result is shown in Table 3.

(used material ) calcium aluminate: main component C<sub>12</sub>A<sub>7</sub>, brain value 6100 cm<sup>2</sup>/g, density 2.90

(measurement method )

Powder amount of dust: blowing after starting, in every 10 min it measured with constant position of 3 m than spraying site.

rebound ratio: blowing after ending, without depositing it measured quantity of spraying concrete which fell, (rebound ratio) = (Blowing weight of spraying concrete which without depositing fell to the simulation tunnel occasion) / calculated from formula of (Blowing weight of spraying concrete which is used) X 100 (%).

[0051]

[Table 3]

Table 3

Exprimment	High Quality De-watering agent	Amount of dust	Rebound rate	Notes
				Carried Out Example [Translator's Note: 16 Entries

[Underneath Table 3]

Parts by weight of the high quality dewatering agent is against 100 parts by weight of cemnt.  
(However, high quality dewatering agent (Carried Out Example) is a converted amount for the solid part).

[0052]

(Working Example 4 )

Mixing cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight, it made spraying concrete, mixing quantity which shows quick setding agent which consists of calcium aluminate in the Table 4 in relation to cement 100 parts by weight it executed other than thing which it makes quick setding characteristic spraying concrete, in same way as the Working Example 3, measured compressive strength.

Result is shown in Table 4.

(measurement method )

Compressive strength: spraying concrete which is manufactured, blowing was done in the pull out form of width 25 cm X length 25 cm and form of vertical 50 cm X side 50 cm X length 20 cm.

Using test sample of pull out form, it measured age 3 hours.

From the pull out form surface pin was covered with spraying concrete, the pin was pulled out from back side of form, pull-out strength of that time was sought, (compressive strength) compressive strength was calculated from formula of = (pull-out strength ) X 4/ (test sample surface area).

After age 1 day test sample of diameter 5 cm X length 10 cm which recovers from form of width 50 cm X length 50 cm X thickness 20 cm was measured with 20 ton pressure resistance machines, compressive strength was sought.

[0053]

[Table 4]

Table 4

Exprimment	Calcium	Compression Strength	Notes
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					Carried Out Example [Translator's Note: 6Entries]

[Underneath Table 4]

h is hours, d is days, parts by weight of the coagulation promotion agent is against 100 parts by weight of cement. " - " under compression strength was impossible to extract because of lack of pressure.

[0054]

(Working Example 5 )

Mixing cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight, it made spraying concrete, 10 parts by weight mixing the quick setting agent which mixes coagulation promotion medicine of quantity which is shown in calcium aluminate 100 parts by weight and Table 5 in relation to cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, followed compressive strength with specified material age to method of Working Example 4 and measured.

Result is shown in Table 5.

[0055]

[Table 5]

Table 5

Exprimnt	Coagulation watering agent	Compression Strength		Notes	
					Carried Out Example [Translator's Note: 18 Entries]

[Underneath Table 5]

\*is a mixed compound with relative parts by weight A:B:C = 4:3:3

h is hours, d is days, and parts by weight of the coagulation promotion agent is against 100 parts by weight of calcium aluminate.

[0056]

(Working Example 6 )

Mixing cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight, it made spraying concrete, quick setting agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, mixing the quantity which shows in Table 6, in relation to cement 100 parts by weight it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, followed compressive strength to method of Working Example 4 and measured.

Result is shown in Table 6.

[0057]

[Table 6]

Exprimment	Coagulation promotion agent	Setding agent			Compression Strength		Notes
							Compression Example
							Carried Out Example [Translator's Note: 12 Entries]

[Underneath Table 6]

\*is a mixed compound with relative parts by weight A:B:C = 4:3:3

h is hours, d is days, and parts by weight of the setding agent is against 100 parts by weight of cement. . " - " under compression strength was impossible to extract because of lack of pressure.

[0058]

(Working Example 7 )

It made unit amount of each material similar to Working Example 1, used coarse aggregate and fine aggregate of chart dry state, mixed cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight and manufactured dry concrete, carried to spraying machine with belt conveyor.

On one hand, 10 parts by weight, were added to dry concrete on belt conveyor quick setding agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight in relation to cement 100 parts by weight.

dry concrete which adds quick setding agent pneumatic transport was done from spraying machine, water way 50 parts by weight ago, in relation to cement 100 parts by weight to execute dry type spraying operation in addition, following compressive strength to method of Working Example 4, was measured due to Y letter tube.

As a result, spraying operation is executed was possible without either plugging or other trouble of pipe.

As for compressive strength of age 3 hours of that time as for compressive strength of 1.3 N/mm<sup>2</sup> 28 days they were 33.4 N/mm<sup>2</sup>

[0059]

Powder amount of dust of this time of also, when it compares with the case where high performance de-watering agent 1 is not added, among when high performance de-watering agent 1 is not added, among when high performance de-watering agent 1 is added in relation to being 29.6 mg/m<sup>3</sup>, with

19.6 mg/m<sup>3</sup>. method which adds high performance de-watering agent 1 clearly powder dust generated amount was less.

[0060]

(Working Example 8 )

Mixing coagulation lag medicine of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10. 3 parts by weight, and Table 7, it made spraying concrete, quick setting agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A 10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, followed compressive strength to method of Working Example 4 and measured.

Result is shown in Table 7.

(used material )

coagulation lag medicine  $\alpha$  : marketing citric acid

coagulation lag medicine  $\beta$  : commercial potassium carbonate

coagulation lag medicine  $\gamma$  : commercial citric acid 3 and blend of potassium carbonate 7 (weight ratio )

coagulation lag medicine  $\delta$  : marketing ethyleneglycol

coagulation lag medicine  $\epsilon$  : marketing sodium tripoly phosphate

coagulation lag medicine  $\zeta$  : marketing sodium borate

[0061]

[Table 7]

Table 7

Exprimment	Coagulation Slowing agent	Compression Strength		Notes	
					Carried Out Example [Translator's Note: 31 Entries]

[Underneath Table 7]

Parts by weight of the coagulation slowing agent is against 100 parts by weight of cement.

[0062]

(Working Example 9 )

Mixing powder dust decreasing agent of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10. 3 parts by weight, and Table 8, it made spraying concrete, quick setding agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setding characteristic spraying concrete, in same way as Working Example 3, measured powder amount of dust and rebound ratio.

Result is shown in Table 8.

(used material )

Powder dust decreasing agent A : marketing methyl cellulose

Powder dust decreasing agent E : marketing hydroxypropyl cellulose

[0063]

[Table 8]

Table 8

Exprimment	Dust decreasing agent	Amount of dust	Rebound rate	Notes
				Carried Out Example [Translator's Note: 9 Entries]

[Underneath Table 8]

Parts by weight of the powder decreasing agent is against 100 parts by weight of cement.

[0064]

(Working Example 10.)

Mixing ultra fine powder of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10. 3 parts by weight, and the Table 9, it made spraying concrete, quick setting agent which mixes the calcium aluminate 100 parts by weight and coagulation promotion medicine A 10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, measured rebound ratio.

Result is shown in Table 9.

(used material )

ultra fine powder a: commercial fumed silica, average particle diameter 10  $\mu$  m or less

ground product, average particle diameter 10  $\mu$  m or less of ultra fine powder b: commercial furnace slag

[0065]  
[Table 9]



Table 9

Exprimint	Ultra fine powder	Rebound rate	Notes
			Carried Out Example [Translator's Note: 15 Entries

[Underneath Table 9]

Parts by weight of the Ultra fine powder is against 100 parts by weight of cement.

[0066]

(Working Example 11)

Mixing fiber of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10. 3 parts by weight, and the Table 10, it made spraying concrete, quick setting agent which mixes the calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, measured impact resistance.

Result is shown in Table 10.

(used material )

fiber i: commercial vinylon fiber, fiber length 10 mm

fiber ii: commercial steel fiber, fiber length 30 mm

(measurement method )

You placed on standard sand which trains those which cut off the spraying concrete after impact resistance: age 3 hours in width 20 cm X length 20 cm X thickness 2.5 cm, to planar sphere of the weight 100g fell from height of 50 cm.

Those which drop times destroys within 5 times were designated as the X, without destroying O, without destroying those where crack enters those where crack does not enter were done © with.

[0067]

[Table 10]

Table 10

Exprimment	Fiber	Impact resistance	Notes
			Carried Out Example [Translator's Note: 7 Entries

[Underneath Table 9]

Parts by weight of the fiber is against 100 parts by weight of cement.

[0068]

(Working Example 12 )

It made quantity which shows unit amount of cement in Table 11, it made quantity which shows amount used of water in Table 11 in relation to cement 100 parts by weight, mixed cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight and made spraying concrete, quick setding agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, mixing 10 parts by weight in relation to cement 100 parts by weight, it executed other than the thing which it makes quick setding characteristic spraying concrete, in the same way as Working Example 3.

Concerning spraying concrete, slump immediately after mixing was measured.

Result is shown in Table 11.

[0069]  
[Table 11]

Table 11

Exprimint	Cement	Water	Slump			Compression Strength		Notes
								Carried Out Example [Translator's Note: 6 Entries]

[Underneath Table 11]

h is hours, d is days, cement amount is  $\text{kg/m}^3$ . Parts by weight of water is against 100 parts by weight of cement.

[0070]

[Effects of the Invention]

Is kneaded spraying concrete with such as trouble of spraying machine and by using the spraying material of this invention, necessity to leave occurring, spraying concrete and quick setting characteristic spraying concrete to which flow property is large over lengthy, is superior in strength manifestation, powder dust decrease, and rebound decrease are acquired.

spraying material of also, this invention because it is a powder, as cement and various cement filler premix be able to designate, be able to improve the workability beforehand, from high quality spraying material can be adjusted.

Furthermore, jointly using with cellulose type powder dust decreasing agent, be able to maintain de-watering effect and dispersing effect, it can hold down also the obstruction of strength manifestation characteristic.

**SPRAYING MATERIAL AND SPRAYING FABRICATION METHOD WHICH  
USES THAT**

[吹付材料及びそれを用いた吹付工法]

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(57) [Abstract]

[Problems to be Solved by the Invention]

Offer of spraying material and spraying fabrication method to which flow property is large,  
is superior in strength manifestation, powder dust decrease, and rebound decrease.

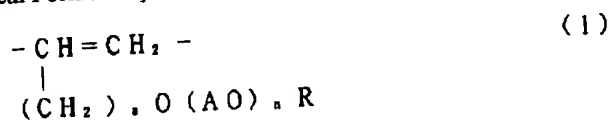
[Means to Solve the Problems]

Spraying material, which contains powder polycarboxylic acid high performance de-  
watering agent which consists of calcium salt of copolymer of polyalkylene glycol mono  
alkenyl ether and maleic acid which are shown with cement and Chemical Formula (1)

a = 0 is desirable in Chemical Formula (1).



[Chemical Formula 4]



(但し、式中のAは炭素数2～4のアルキレン基であり、

Rは水素又は炭素数1～4のアルキル基であり、aは0又

は1、nは1～60の整数である)

Translator's Notes: [Chemical Formula 4]

(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

Spraying material, quick setting agent, coagulation promotion medicine, and coagulation lag medicine which designate calcium aluminate as main component, may contain mulling agent such as powder dust decreasing agent, ultra fine powder, and fiber.

[Claim(s)]

[Claim 1]

Containing powder polycarboxylic acid high performance de-watering agent which consists of calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with cement and Chemical Formula (1) spraying material, which becomes and makes feature

[Chemical Formula 1]



(但し、式中のAは炭素数2～4のアルキレン基であり、

Rは水素又は炭素数1～4のアルキル基であり、aは0又

は1、nは1～60の整数である)

Translator's Notes: [Chemical Formula 1]

(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

[Claim 2]

Containing powder polycarboxylic acid high performance de-watering agent, and calcium

aluminate which consist of calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with cement, Chemical Formula (1) containing quick setting agent which becomes, spraying material, which is stated in Claim 1 or 2 which becomes and makes feature

[Claim 3]

It is a  $a=0$  in Chemical Formula (1) and spraying material, which is stated in the Claim 1 or 2 which is made feature

[Claim 4]

Furthermore, quick setting agent containing coagulation promotion medicine, spraying material, which is stated in Claim 1~3 which becomes and makes feature

[Claim 5]

Furthermore, coagulation lag medicine, containing mulling agent of one, two or more kinds which is chosen from powder dust decreasing agent, ultra fine powder, and group which consists of fiber spraying material, which is stated in Claim 1~4 which becomes and makes feature

[Claim 6]

Using spraying material which is stated in Claim 1~5, spraying fabrication method, which becomes and makes feature

[Description of the Invention]

[0001]

[Technological Field of Invention]

this invention contains specific powder polycarboxylic acid high performance de-watering agent, blowing regards the spraying material and spraying fabrication method which uses that to ground aspect which is exposed in road, railroad, and derived water line or other tunnel.

Furthermore, with this invention, generic doing dry cement mortar, cement mortar, paste, and concrete, you call cement mortar or concrete.

[0002]

[Prior Art]

Until recently, tunnel excavation, etc., spraying fabrication method of quick setting characteristic concrete which combines quick setting agent to the concrete in order to prevent fall of ground which is exposed is done, (Japan Examined Patent Publication Sho 52-4149 disclosure).

Usually, it installed this fabrication method, in excavation construction site, it makes spraying concrete with weighing mixed plant of cement aggregate and water, conveys that by agitator car, pneumatic transport does with concrete pump, with confluence tube, which is provided on middle, it mixes with quick setting agent which pneumatic transport is done from other, Until on ground aspect it becomes predetermined thickness, as quick setting characteristic spraying concrete blowing it is a fabrication method.

With this fabrication method in order to give flow property to spraying concrete, when manufacturing spraying concrete, adds high performance de-watering agent which possesses de-watering property, air permeability, and the ability to disperse is.

As high performance de-watering agent, you can list naphthalene sulfonate system, melamine sulfonate system, and polycarboxylic acid system etc.

Mixing to various cement filler as powder, you can use high performance de-watering agent of naphthalene sulfonate type and melamine sulfonate type, for spraying material.

But, high performance de-watering agent of naphthalene sulfonate type, when it jointly uses with powder dust decreasing agent and rebound preventing agent of cellulose type, had deficiency that de-watering property, air permeability, and the ability to disperse disappears.

Deficiency that there was a high performance de-watering agent of naphthalene sulfonate type and melamine sulfonate type the improved effect of intensity is small together.

Furthermore, spraying concrete which is manufactured is kneaded and when it leaves, change over time of slump is large, kneads spraying concrete with the mechanical/ electrical trouble, etc., of blowing apparatus and when necessity to leave occurs, the concrete becomes hard, causes adverse effect to pneumatic transport behavior, becomes difficult, to mix to quick setting agent and uniform becomes non-uniform quick setting characteristic spraying concrete in qualitative. There was a deficiency that or other hazard where concrete falls from tunnel surface occurs.

[0003]

Then, it reached point where polycarboxylic acid high performance de-watering agent where slump loss is small is used.

flow property of spraying concrete and method which improves quick setting characteristic are proposed as polycarboxylic acid high performance de-watering agent, polyalkylene glycol mono allyl ether-maleic acid copolymer, polyalkylene glycol mono (meth) acrylic acid ester- (meth) acrylic acid copolymer, water soluble olefin and  $\alpha$  and  $\beta$ -unsaturated by using saponate, of copolymer, sulfonation styrene-maleic acid copolymer of di-carboxylic acid derivative and saponate etc of the styrene-maleic acid copolymer, etc., (Japan Examined Patent Publication Hei 5-53743 disclosure, Japan Unexamined Patent Publication Hei 3-153550 disclosure ).

[0004]

#### [Problems to be Solved by the Invention]

But, these polycarboxylic acid high performance de-watering agent were not something which still is satisfied in point of water reduction ratio, slump loss, and strength manifestation.

As for de-watering agent in order without adding not to have with spraying site, it is a powder which premix can be made various powder body material beforehand, it is desirable, but conventional polyalkylene glycol (meth) acrylic acid ester- (meth) acrylic acid copolymer, usually unless in wax state and malt syrup condition, it is a aqueous solution with room temperature, had problem that cannot be used.

Because of that, cement, quick setting agent or other powder cement mulling agent, and fly ash or other powder cement filler and the de-watering agent with site weighing/ must be added specially separately in spraying job, there was a problem that workability decreases considerably.

Then, ability to disperse, quick setting characteristic, it reached point where it can seek spraying material which it can be satisfied from point of the intensity, and workability.

[0005]

As for this inventor, as for result which these problem various was examined, by using specific powder polycarboxylic acid high performance de-watering agent which premix can be made portland cement, alumina cement, and mulled cement or other various cement, silica fume, furnace slag, and fly ash or other various cement filler, and other powder high performance de-watering agent, powder dust decreasing agent, powder foam inhibitor, coagulation promotion medicines, and coagulation lag medicine or other various powder cement mulling agent or other various powder body material beforehand, slump retention, quick setting characteristic, Obtaining knowledge where strength manifestation characteristic, powder dust low degradation, rebound characteristic of initial stage/long period, and high quality spraying material which is superior in workability are acquired, this invention it reached to completion.

[0006]

[Means to Solve the Problems]

Namely it is a spraying material where this invention becomes and containing powder polycarboxylic acid high performance de-watering agent which consists of calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and the maleic acid which are shown with cement and Chemical Formula (1) makes feature.

[Chemical Formula 2]



(但し、式中のAは炭素数2~4のアルキレン基であり、

Rは水素又は炭素数1~4のアルキル基であり、aは0又

は1、nは1~60の整数である)

Translator's Notes: [Chemical Formula 2]

(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1~ 60).

And, containing powder polycarboxylic acid high performance de-watering agent, and calcium aluminate which consist of the calcium salt of copolymer of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with the cement, Chemical Formula (1) containing quick setting agent which becomes, with the spraying material which is stated in Claim 1 or 2 which becomes and makes feature, it is a a=0 in Chemical Formula (1) and with said spraying material which is made feature, furthermore, Quick setting agent containing coagulation promotion medicine, with said spraying material which becomes and makes feature, furthermore, coagulation lag medicine, containing mulling agent of one, two or more kinds which is chosen from the powder dust decreasing agent, ultra fine powder,, and group which consists of fiber with said spraying material which becomes and makes feature, using said spraying material, it is a spraying fabrication method which becomes and makes feature.

[0007]

[Embodiment of the Invention]

Below, this invention is explained in detail.

[0008]

Usually it is marketed as cement which is used with this invention, normally, quickly you can list various mulled cement, and commercial fine particle cement, etc., which mix fly ash and furnace slag, etc., to these portland cement of strong, midrange heating, and super

quickly strong or other various portland cement, to fine powder convert various portland cement and various mulled cement and are possible to use.

[0009]

Powder polycarboxylic acid high performance de-watering agent which is used with this invention is calcium salt of copolymer of polyalkylene glycol alkenyl ether and maleic acid which are shown with below-mentioned Chemical Formula (1), (You call main copolymer calcium salt below).

[Chemical Formula 3]



(但し、式中のAは炭素数2～4のアルキレン基であり、

Rは水素又は炭素数1～4のアルキル基であり、aは0又

は1、nは1～60の整数である)

Translator's Notes: [Chemical Formula 3]

(However, "A" in the equation is alkylene base with 2 to 4 carbons. "R" is alkylene base with 1 ~ 4 hydrogens or carbons, "a" is 0 or 1, and n is an integral number from 1 ~ 60).

[0010]

In the aforementioned Chemical Formula (1), in A ethylene group of carbon number 2 is desirable in point where water solubility of this copolymer calcium salt is large.

As for alkyl group which is shown with R production of copolymer being easy, methyl group is desirable in point where water solubility is large.

n 1 - 60 is desirable in point of ability to disperse.

When it is under 1, ability to disperse is not acquired, when, it exceeds 60, viscosity of reaction mixture becomes large at time of copolymer production, there is a possibility reactivity becoming small.

[0011]

Weight average molecular weight of this copolymer calcium salt 3000 - 100000 is desirable.

When it is under 3000, ability to disperse to decrease, exceed 100000 and not be able to expect further effect, there is a possibility of becoming the high cost.

Weight average molecular weight designated for example known polyethylene glycol as standard substance, used those which were measured due to aqueous system GPC.

[0012]

It can produce copolymer (You call main copolymer below) of polyalkylene glycol mono alkenyl ether and maleic acid which are shown with Chemical Formula (1) with

manufacturing method of public knowledge.

With method which is stated in for example Japan Unexamined Patent Publication Showa 64- 109 disclosure and Japan Unexamined Patent Publication Hei 8-46652 disclosure, in the organic solvent and under condition of without any solvents, radical polymerization doing copolymer and polyalkylene glycol mono vinyl ether of polyalkylene glycol mono allyl ether and maleic anhydride and copolymer of maleic anhydride, with radical initiator, it can produce.

In polyalkylene glycol mono alkenyl ether which is used for this copolymer, it is superior in copolymeriz-ability, productivity, and de-watering property of maleic anhydride, polymerization rate is quick, and, in point which can remove not reacted impurity in copolymer which is acquired easily, the polyalkylene glycol mono vinyl ether which is a  $\alpha=0$  in Chemical Formula (1) is desirable.

Furthermore, as for copolymerization mole ratio of polyalkylene glycol alkenyl ether and the maleic anhydride, in point where copolymer is acquired easily,  $\frac{1}{2} - 2/1$  is desirable,  $1/1.2 - 1.2/1$  is more desirable.

It is possible to use citraconic acid anhydride and maleimide in place of also, maleic anhydride, but maleic anhydride is desirable in point of ability to disperse and cost.

[0013]

This copolymer calcium salt is acquired this copolymer and calcium salt compound by reacting.

As manufacturing method, in solution which organic solvent solution and copolymer of copolymer heating and melting is done, adding slurry which mixes calcium hydroxide and the calcium hydroxide and water, neutralization reaction after doing, drying/ powder fragment the method of doing. organic solvent of copolymer stripping doing with heated steam, you can list method etc which after recovering, reacting with calcium hydroxide, the drying/ powder fragment does copolymer aqueous solution.

[0014]

average particle diameter of powder polycarboxylic acid high performance de-watering agent which consists of this copolymer calcium salt especially is not limited.  $0.1 - 200 \mu m$  are desirable.

0.1 When it is under the  $\mu m$ , cost which making fine particles is done to become high, when it exceeds  $200 \mu m$ , powder polycarboxylic acid high performance de-watering agent without melting rapidly, various powder body material and segregation doing the occasion where dry blend it does there is a possibility effect not being acquired.



fine powdering is done powder polycarboxylic acid high performance de-watering agent as method which usually, you can list powder mist drying, powder fragment, and solvent precipitation etc.

[0015]

As for amount used of powder polycarboxylic acid high performance de-watering agent which consists of main copolymer calcium salt of Chemical Formula (1) 0.01 - 5.0 parts by weight are desirable in relation to cement 100 parts by weight, 0.02- 5.0 parts by weight are more desirable.

0.01 When under part by weight satisfactory dispersing performance is not acquired, exceeds 5.0 parts by weight there is a possibility of causing coagulation lag and material separation.

[0016]

Because it is a polycarboxylic acid high performance de-watering agent of powder, you can use main copolymer calcium salt of Chemical Formula (1) as various cement, various cement filler, and premix product which is mixed with various powder cement mulling agent beforehand.

Effect of powder dust decrease and rebound prevention can be granted by mixing to quick setting agent which consists of for example calcium aluminate and the alkali metal aluminate and alkali metal carbonate salt or other coagulation promotion medicine beforehand.

[0017]

With this invention, in point which causes coagulation of cement mortar or concrete in initial stage, uses calcium aluminate as quick setting agent is desirable.

calcium aluminate calls quick setting component which causes coagulation of the concrete in initial stage, powder fragment are done those etc which can list the calcium aluminate heat treated substance which when  $C_3A$ ,  $Al_2O_3$  is designated as A, is shown the CaO with  $C_3A$ ,  $C_{12}A_7$ , CA, and  $CA_2$  etc as mineral component.

Furthermore,  $C_{11}A_7$ / Ca  $X_2$  which replaces CaO of one of the aluminosilicate,  $C_{12}A_7$  which contains  $SiO_2$  as other mineral component, with Ca  $F_2$  or other halide (As for X fluorine or other halogen),  $C_4A_3$ /  $SO_3$ , alumina cement, and sodium, potassium, and part solid solution is done calcium aluminate etc which include  $SO_3$  component you can list lithium or other alkali metal, can use crystalline and amorphous in each case.

Among these, in point of reactivity, amorphous calcium aluminate which heat treated substance which corresponds to  $C_{12}A_7$  composition quench is done is desirable.

As for granularity of calcium aluminate, in quick setting characteristic and the initial stage strength manifestation characteristic point, 3000 cm<sup>2</sup>/g or more are desirable at brain value, 4000 cm<sup>2</sup>/g or more are more desirable.

When it is under 3000 cm<sup>2</sup>/g, there is a possibility quick setting characteristic and initial stage strength manifestation characteristic decreasing.

[0018]

As for amount used of calcium aluminate, 1 - 20 parts by weight are desirable in relation to cement 100 parts by weight, 5 - 15 parts by weight are more desirable.

When under 1 part by weight initial stage coagulation does not happen, exceeds 20 parts by weight there is a possibility of obstructing long period strength manifestation characteristic.

[0019]

With this invention, promoting coagulation of cement, in point which gives quick setting power to cement mortar, uses coagulation promotion medicine is desirable.

[0020]

As coagulation promotion medicine, sodium aluminate, potassium aluminate, and aluminic acid lithium or other alkali metal aluminate, sodium carbonate, potassium carbonate, and lithium carbonate or other alkali metal carbonate salt, you can list sodium hydroxide, potassium hydroxide, and lithium hydroxide or other alkali metal hydroxide, sodium sulfate, potassium sulfate, aluminum sulfate, and alum or other sulfate, hydrated lime, and amine compound, etc are possible to jointly use these one, two or more kinds.

Among these in coagulation characteristic point, use of alkali metal aluminate and alkali metal carbonate salt is desirable.

With this invention, in point of improvement of initial stage coagulation characteristic and strength manifestation characteristic, calcium aluminate and coagulation promotion medicine are jointly used are desirable.

Furthermore, when depending, melting in water, it is possible to use coagulation promotion medicine as liquid.

[0021]

As for amount used of coagulation promotion medicine, when calcium aluminate is not jointly used, 1 - 20 parts by weight are desirable in relation to cement 100 parts by weight, 5 - 15 parts by weight are more desirable.

When under 1 part by weight coagulation of cement mortar does not promote, exceeds 20 parts by weight there is a possibility of causing adverse effect to long period strength manifestation characteristic.

[0022]

When also, calcium aluminate is jointly used, as for amount used of coagulation promotion medicine, 0.5 - 50 parts by weight are desirable in relation to calcium aluminate 100 parts by weight, 1 - 30 parts by weight are more desirable.

0.5 When under parts by weight coagulation of cement mortar does not promote, exceeds 50 parts by weight there is a possibility of causing adverse effect to long period strength manifestation characteristic.

[0023]

As for amount used of quick setting agent when calcium aluminate and the coagulation promotion medicine are mixed, 1 - 20 parts by weight are desirable in relation to the cement 100 parts by weight, 5 - 15 parts by weight are more desirable.

When under 1 part by weight coagulation of cement mortar does not promote, exceeds 20 parts by weight there is a possibility of obstructing long period strength manifestation.

[0024]

With this invention, furthermore, coagulation lag medicine, uses mulling agent of the one, two or more kinds which is chosen from ultra fine powder, powder dust decreasing agent and group which consists of fiber is desirable.

[0025]

coagulation lag medicine has influence which setting time of cement mortar the delay is done, organic acid, alkali metal carbonate salt, can list alcohols, phosphate, and borate etc.

[0026]

As organic acid, you can list gluconic acid, tartaric acid, citric acid, malic acid, and lactic acid or these salt etc.

As for amount used of organic acid, 0.05 - 3 parts by weight are desirable in relation to cement 100 parts by weight, 0.1 - 2 parts by weight are more desirable.

0.05 When under parts by weight there is not an effect, exceeds 3 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0027]

As alkali metal carbonate salt, you can list sodium carbonate, potassium carbonate, sodium bicarbonate, and potassium hydrogen carbonate etc.

As for amount used of alkali metal carbonate salt, 0.1 - 10 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 5 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 10 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0028]

As alcohols, propylene oxide and water soluble polymer polyols etc which is a adduct which the ethylene oxide addition polymerization is done can list low molecular weight water soluble alcohol and to polyethylene glycol or polypropylene glycol or other polyalkylene glycols and the triethanolamine or other amino alcohols which one or greater it possesses ethanol, methanol, ethyleneglycol, and glycerine or other hydroxy group.

As for amount used of alcohols 0.1 - 5 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 3 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 5 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0029]

As phosphate, you can list monosodium phosphate, disodium phosphate, trisodium phosphate, sodium hexametaphosphate, sodium tripolyphosphate, and tri sodium metaphosphate etc.

It is possible to use potassium in place of also, sodium.

Among these, in point which is difficult to obstruct long period strength manifestation characteristic, sodium tripolyphosphate is desirable.

As for amount used of phosphate, 0.1 - 5 parts by weight are desirable in relation to cement 100 parts by weight, 0.2 - 2 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 5 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0030]

As borate, you can list sodium borate and potassium borate etc.

As for amount used of borate 0.1 - 10 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 5 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 10 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0031]

In these coagulation lag medicines in point of initial stage strength manifestation, combined use of organic acid and alkali carbonate is desirable.

[0032]

When organic acid and alkali carbonate are jointly used, as for amount used of the alkali carbonate, 10 - 1000 parts by weight are desirable in relation to organic acid 100 parts by weight, 50 - 700 parts by weight are more desirable.

When under 10 parts by weight there is not an effect, exceeds 1000 parts by weight there is a possibility delayed decreasing.

As for amount used of blend of organic acid and alkali carbonate, 0.1 - 10 parts by weight are desirable in relation to cement 100 parts by weight, 0.5 - 5 parts by weight are more desirable.

When under 0.1 weight sections there is not an effect, exceeds 10 parts by weight hardening doing too much, delay there is a possibility of becoming poor curing.

[0033]

Powder dust decreasing agent which is used with this invention has powder dust low degradation and influence which possesses rebound prevention property, methyl cellulose,

hydroxypropyl cellulose, ethyl cellulose, methylethyl cellulose, you can list polyvinyl alcohol, polyacrylic acid, polyvinyl acetate, and polyethylene-polyvinyl acetate copolymer etc.

Among these, in point whose effect is large, methyl cellulose is desirable.

As for amount used of powder dust decreasing agent, 0.001 - 1.0 parts by weight are desirable in relation to cement 100 parts by weight, 0.01 - 0.5 parts by weight are more desirable.

0.001 When under part by weight there is not an effect, exceeds 1.0 parts by weight there is a possibility viscosity becoming large, causing hindrance to pneumatic transport behavior.

[0034]

ultra fine powder which is used with this invention has influence of average particle diameter 10  $\mu$  m or less, decrease of amount of cement and powder amount of dust and improvement of pneumatic transport behavior of concrete are made possible.

As ultra fine powder, fine powder slag, fly ash, bentonite (DANA 71.3.1a.1-2 ), you can list kaolin, and silica fume etc.

Among these in point whose effect is large, silica fume is desirable.

As for amount used of ultra fine powder, 1 - 100 parts by weight are desirable in relation to cement 100 parts by weight, 2 - 30 parts by weight are more desirable.

When under 1 part by weight there is not an effect, exceeds 100 parts by weight there is a possibility coagulation and hardening being late.

[0035]

fiber which is used with this invention be able to use inorganic and organic in each case, impact resistance and elasticity of spraying concrete it is something which improves.

As for length of fibrous substance, in point of pneumatic transport behavior and the compatibility, 50 mm or less are desirable, 30 mm or less is more desirable.

When it exceeds 50 mm, there is a possibility spraying concrete being plugged in pneumatic transport.

As fiber of inorganic, you can list glass fiber, carbon fiber, rock wool, asbestos, ceramic

fiber, and metal fiber, etc you can list vinylon fiber, polyethylene fiber, polypropylene fiber, poly acrylic fiber, cellulose fiber, polyvinyl alcohol fiber, polyamide fiber, pulp, linen, wooden wool, and wood chip etc as fiber of organic.

Among these, vinylon fiber and metal fiber are desirable in point of the economy.

As for amount used of fiber, 0.5 - 7 parts by weight are desirable in relation to cement 100 parts by weight, 1 - 5 parts by weight are more desirable.

0.5 When under parts by weight there is not an effect, exceeds 7 parts by weight there is a possibility flow property of spraying concrete decreasing.

[0036]

As for amount used of water with this invention, 35 - 60 parts by weight or less are desirable in relation to cement 100 parts by weight, 40 - 55 parts by weight are more desirable.

When it is under 35 parts by weight, not be able to mix with mixer, when it exceeds 60 parts by weight, there is a possibility strength manifestation characteristic becoming bad.

[0037]

As for coarse aggregate and fine aggregate or other aggregate which are used with this invention moisture absorption being low, those where aggregate intensity is high are desirable, but it is not something which especially is restricted.

Those of maximum diameter 20 mm or less are desirable as coarse aggregate, when pumping behavior is considered, those of maximum diameter 5~15 mm are more desirable.

Those of maximum diameter 5 mm or less are desirable as fine aggregate, can list river sand, pit sand, lime sand, and silica sand etc.

[0038]

When using spraying material of this invention, it is possible to use foam inhibitor in order to adjust taking amount of air.

As foam inhibitor, lower alcohols, higher alcohol, oils, fatty acids, fatty acid esters, phosphate ester, metal soap, mineral oil, silicones, and polymer etc of polyethers are listed.

Among these polymer is desirable in point whose effect is large.

As polymer, portion of end group of polyoxyethylene polypropylene adduct or other polyoxy alkylene and polyoxy alkylene with the alkyl group etherification portion of end group of polyoxy alkylene alkyl ethers, polyoxy alkylene which are done with aryl group and alkyl aryl group etherification polyoxy alkylene (alkyl) aryl ether sulfuric acid ester salt which portion of end group of polyoxy alkylene fatty acid esters, polyoxy alkylene which portion of end group of polyoxy alkylene (alkyl) aryl ethers, polyoxy alkylene which are done fatty acid esterification are done sulfuric acid esterification are done, And amination are done polyoxy alkylene alkyl amines or other polyoxy alkylene etc which can list portion of the end group of polyoxy alkylene.

As method of use of foam inhibitor, method of adding beforehand in the middle which produces this copolymer calcium salt. Impregnating foam inhibitor in white carbon, and silica or other inorganic powder body the method of making powder foam inhibitor. And you can list this copolymer calcium salt and with various powder body material the method etc which premix is done.

[0039]

As for amount used of foam inhibitor, 0.01 – 10 parts by weight are desirable in relation to powder polycarboxylic acid high performance de-watering agent 100 parts by weight which consists of this copolymer calcium salt, 0.05 - 5 parts by weight are more desirable.

0.01 When it is under part by weight, there not to be a de-foaming effect, exceed 10 parts by weight and not be able to expect improvement of de-foaming effect, there is a possibility taking amount of air rather becoming many.

[0040]

With spraying fabrication method of this invention, you work spraying from property, economy, and the ability to fabricate, etc., which are required, as dry cement mortar, cement and contain water the cement mortar, paste, and concrete which contain cement, it is possible, while flowing confluent mixing it is possible to do quick setting agent which contains calcium aluminate in according to need, these.

[0041]

As spraying fabrication method, you can list dry type spraying method and wet type spraying method.

As dry type spraying method, although dry cement mortar which mixes cement and the aggregate is manufactured, also according to need quick setting agent carries mixes with belt conveyor, pneumatic transport does, supplies quick setting agent, water to order midway and blowing can list method etc.



As wet type spraying method, it manufactures cement mortar which mixes cement, aggregate, and water pneumatic transport does, pneumatic transport it does according to need quick setting agent from one side of Y letter tube which is provided on the for example middle can list cement mortar and confluent mixing does and blowing method etc.

In case of these spraying fabrication method, powder polycarboxylic acid high performance de-watering agent, coagulation promotion medicine and coagulation lag medicine which consist of this copolymer calcium salt, be able to mix mulling agent and the filler other than quick setting agent such as powder dust decreasing agent, ultra fine powder, and fiber, on both side of mortar side and quick setting agent side, pneumatic transport is good doing in only one side, to jointly use to both sides is possible.

If it can blow spraying material which consists of finally this invention there is not a problem.

coagulation promotion medicine, in point where effect which is superior is acquired, uses powder dust decreasing agent, ultra fine powder, and fiber, to mortar side is desirable.

Furthermore, when depending, it mixes quick setting agent and the water, it is possible to use as quick setting agent slurry.

[0042]

Regarding spraying fabrication method of this invention, you can use spraying facility, etc., of past use.

As for usually, as for spraying pressure 2 - 5 kg/cm<sup>2</sup>, spraying velocity they are 4 - 20 m<sup>3</sup>/h.

If spraying facility spraying is done in fully, it is not something which especially is limited, ants bar corporation trade name "ants bar 280" etc., you can use quick setting agent pneumatic conveyor equipment "Natom Creet," etc., to pneumatic transport of quick setting agent in pneumatic transport of for example concrete.

[0043]

[Working Example(s)]

this invention is explained in detail below, on basis of Working Example.

[0044]

(Working Example 1 )

It designated unit amount of each material as cement 360 kg/m<sup>3</sup>, coarse aggregate 734 kg/m<sup>3</sup>, fine aggregate 1089 kg/m<sup>3</sup>, and water 191 kg/m<sup>3</sup>, mixing high performance de-watering agent of quantity which is shown in Table 1, in relation to cement 100 parts by weight it made spraying concrete.

Concerning this spraying concrete, slump and compressive strength were measured.

However, n of main copolymer calcium salt in used material is n in the Chemical Formula (1).

Result is shown in Table 1.

[0045]

(used material )

cement: marketing normally portland cement density 3.16

coarse aggregate: Toyama Prefecture Sakaigawa product gravel, chart dry state, maximum size 15 mm or less, density 2.64

fine aggregate: Toyama Prefecture Sakaigawa product river sand, chart dry state, maximum size 5 mm or less, density 2.61

Water: tap water, 20 deg C

Main copolymer calcium salt, methoxy polyethylene glycol vinyl ether-maleic acid copolymer calcium salt, n=45, weight average molecular weight 20000, powder body of high performance de-watering agent 1:, particle diameter 200  $\mu$  m or less

Main copolymer calcium salt, methoxy polyethylene glycol vinyl ether-maleic acid copolymer calcium salt, n=10, weight average molecular weight 20000, powder body of high performance de-watering agent 2:, particle diameter 200  $\mu$  m or less

Main copolymer calcium salt, methoxy polyethylene glycol allyl ether-maleic acid copolymer calcium salt, n=10, weight average molecular weight 20000, powder body of high performance de-watering agent 3:, particle diameter 200  $\mu$  m or less

high performance de-watering agent 4: commercial naphthalene sulfonate high performance de-watering agent, powder body

high performance de-watering agent 5: commercial melamine high performance de-watering agent, powder body high performance de-watering agent 6: commercial methoxy polyethylene glycol methacrylic acid ester

-methacrylic acid copolymer salt high performance de-watering agent, aqueous solution which is made main component

high performance de-watering agent 7: styrene-maleic acid copolymer salt, weight average proportion 40000, powder body, particle diameter 200  $\mu$  m or less

[0046]

(measurement method )

ス	ラ	ブ:J		S	A		0	According to	て Measurement.
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Pouring in Lee jp7, it formed, after hardening mold removal did, the curing in water did with 20 deg C, measured with 20 t pressure resistance test machines.

It measured due to weight average molecular weight: aqueous system GPC.

weight average molecular weight designated known polyethylene glycol as standard substance.

[0047]

[Table 1]

実験 No.	高性能 減水剤	スランプ (cm)			圧縮強度 (N/mm <sup>2</sup> )		備考
		直後	30分	60分	7日	28日	
1- 1	0	-	-	-	17.5	38.8	比較例
1- 2	① 0.01	5.0	4.0	2.0	17.6	39.0	実施例
1- 3	① 0.02	5.5	5.0	3.0	17.5	38.7	実施例
1- 4	① 0.05	5.5	5.0	3.5	17.5	38.7	実施例
1- 5	① 0.1	11.0	10.0	9.5	17.4	38.5	実施例
1- 6	① 0.3	17.0	17.5	17.0	17.2	38.5	実施例
1- 7	① 0.5	21.0	21.0	20.5	17.3	38.4	実施例
1- 8	① 1.0	24.5	25.0	25.0	17.0	38.2	実施例
1- 9	① 3.0	>25	>25	>25	16.6	37.5	実施例
1-10	① 5.0	>25	>25	>25	16.0	37.0	実施例
1-11	② 0.3	17.5	17.0	16.5	17.0	38.9	実施例
1-12	③ 0.3	14.5	12.0	9.5	16.5	38.4	実施例
1-13	③ 0.5	17.0	15.5	12.0	14.1	35.1	実施例
1-14	④ 0.3	12.0	5.0	-	17.0	36.8	比較例
1-15	⑤ 0.3	11.0	3.0	-	17.1	38.2	比較例
1-16	⑥ 0.3	14.0	10.5	6.5	16.0	36.2	比較例
1-17	⑦ 0.3	11.5	9.5	5.5	16.2	35.8	比較例

高性能減水剤はセメント100重量部に対する重量部（但し、高性能減水剤⑥は固形分換算値）、圧縮強度の-は強度不足で採取不能。

Table 1

Expriment	High Quality De- watering agent	Slump			Compression Strength		Notes
		Right After	30 Minutes	60 Minutes	7 Days	28 Days	
							Compression Example
							Carried Out Example [Translator's Note: 12 Entries]
							ComparisonExaple [Translator'sNote: Last For Entries]

[Underneath Table 1]

Parts by weight of the high quality dewatering agent is against 100 parts by weight of cemnt.  
(However, high quality dewatering agent (30 Minutes) is a converted amount for the solid part). “ - “  
Water compression strenght was impossible to extract because of lack of pressure.

[0048]

(Working Example 2)

Mixing coagulation promotion medicine of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10.3 parts by weight, and Table 2, it executed other than thing which it makes the spraying concrete, in same way as Working Example 1.

Result is shown in Table 2.

(used material )

coagulation promotion medicine A: marketing sodium aluminate

coagulation promotion medicine B: marketing sodium carbonate

Coagulation promotion medicine C: marketing alum

[0049]

[Table 2]

実験 No.	凝結 促進剤	圧縮強度 (N/mm <sup>2</sup> )				備考
		3h	1d	7d	28d	
1-6	0	0	-	17.2	38.5	実施例
2-1	A 1	<0.1	-	17.0	39.4	実施例
2-2	A 5	<0.1	-	17.4	37.3	実施例
2-3	A10	0.1	-	17.3	30.6	実施例
2-4	A15	0.2	-	17.5	28.8	実施例
2-5	A20	0.2	-	17.8	26.1	実施例
2-6	B 1	<0.1	-	18.9	38.0	実施例
2-7	B 5	0.1	-	17.6	36.1	実施例
2-8	B10	0.1	-	17.2	30.5	実施例
2-9	B15	0.2	-	17.0	25.9	実施例
2-10	B20	0.3	-	17.1	24.8	実施例
2-11	C10	0.1	-	17.6	31.3	実施例
2-12	A5, B5	0.3	9.8	17.6	35.9	実施例
2-13	A5, C5	0.2	10.2	18.3	36.2	実施例
2-14	B5, C5	0.2	11.0	17.9	35.7	実施例
2-15	A4, B3, C3	0.3	11.2	18.0	36.9	実施例

hは時間、dは日、凝結促進剤はセメント100重量部に対する重量部、圧縮強度の-は強度不足で採取不能。

Table 2

Exprimment	Coagulation watering agent	Compression Strength		Notes	
					Carried Out Example [Translator's Note: 16 Entries]

[Underneath Table 2]

h is hours, d is days, parts by weight of the coagulation promotion agent is against 100 parts by weight of cement. " – " under compression strength was impossible to extract because of lack of pressure.

[0050]

(Working Example 3 )

It designated unit amount of each material as cement 360 kg/m<sup>3</sup>, coarse aggregate 734 kg/m<sup>3</sup>, fine aggregate 1089 kg/m<sup>3</sup> and water 191 kg/m<sup>3</sup>, mixing high performance de-watering agent 1 of quantity which is shown in Table 3, in relation to cement 100 parts by weight it made spraying concrete, pneumatic transport it did this making use of concrete pneumatic transport machine "ants bar 280".

From one side of Y letter tube which is provided midway, 10 parts by weight mixing in relation to cement 100 parts by weight, pneumatic transport it did quick setting agent which consists of calcium aluminate, with quick setting agent addition machine "Denkanatom Creet," confluent mixing did and manufactured quick setting characteristic spraying concrete.

This quick setting characteristic spraying concrete with spraying velocity of 4 m<sup>3</sup>/h blowing was done in simulation tunnel of 30 min height 3.5m, width 2.5m, powder amount of dust and rebound ratio were measured.

Result is shown in Table 3.

(used material ) calcium aluminate: main component C<sub>12</sub>A<sub>7</sub>, brain value 6100 cm<sup>2</sup>/g, density 2.90

(measurement method )

Powder amount of dust: blowing after starting, in every 10 min it measured with constant position of 3 m than spraying site.

rebound ratio: blowing after ending, without depositing it measured quantity of spraying concrete which fell, (rebound ratio) = (Blowing weight of spraying concrete which without depositing fell to the simulation tunnel occasion) / calculated from formula of (Blowing weight of spraying concrete which is used) X 100 (%).

[0051]

[Table 3]

実験 No.	高性能 減水剤	粉塵量 (mg/m <sup>3</sup> )	リバウンド率 (%)	備考
3-1	① 0	20.9	22.4	比較例
3-2	① 0.01	20.2	20.2	実施例
3-3	① 0.02	17.8	20.0	実施例
3-4	① 0.05	15.6	19.4	実施例
3-5	① 0.1	14.4	17.7	実施例
3-6	① 0.3	12.1	15.5	実施例
3-7	① 1.0	8.8	5.2	実施例
3-8	① 3.0	5.0	3.0	実施例
3-9	① 5.0	1.6	2.8	実施例
3-10	② 0.3	5.0	14.8	実施例
3-11	③ 0.3	18.0	18.8	実施例
3-12	④ 0.3	18.7	19.2	比較例
3-13	⑤ 0.3	16.9	20.1	比較例
3-14	⑥ 0.3	19.0	19.4	比較例
3-15	⑦ 0.3	19.2	18.3	比較例

高性能減水剤はセメント100重量部に対する重量部（但し、高性能減水剤⑥は固形分換算値）。

Table 3

Exprimment	High Quality De-watering agent	Amount of dust	Rebound rate	Notes
				Carried Out Example [Translator's Note: 16 Entries

[Underneath Table 3]

Parts by weight of the high quality dewatering agent is against 100 parts by weight of cement.  
(However, high quality dewatering agent (Carried Out Example) is a converted amount for the solid part).

[0052]

(Working Example 4)

Mixing cement 100 parts by weight and high performance de-watering agent 10.3 parts by weight, it made spraying concrete, mixing quantity which shows quick setting agent which consists of calcium aluminate in the Table 4 in relation to cement 100 parts by weight it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as the Working Example 3, measured compressive strength.

Result is shown in Table 4.

(measurement method )

Compressive strength: spraying concrete which is manufactured, blowing was done in the pull out form of width 25 cm X length 25 cm and form of vertical 50 cm X side 50 cm X length 20 cm.

Using test sample of pull out form, it measured age 3 hours.

From the pull out form surface pin was covered with spraying concrete, the pin was pulled out from back side of form, pull-out strength of that time was sought, (compressive strength) compressive strength was calculated from formula of = (pull-out strength ) X 4/ (test sample surface area).

After age 1 day test sample of diameter 5 cm X length 10 cm which recovers from form of width 50 cm X length 50 cm X thickness 20 cm was measured with 20 ton pressure resistance machines, compressive strength was sought.

[0053]

[Table 4]

実験 No.	カルシウム ルミネート	圧縮強度 (N/mm <sup>2</sup> )				備考
		3h	1d	7d	28d	
4- 1	0	0	-	17.2	38.5	実施例
4- 2	1	<0.1	-	17.4	37.6	実施例
4- 3	5	0.3	9.9	17.8	36.3	実施例
3- 6	10	0.5	10.8	18.4	31.2	実施例
4- 4	15	0.6	11.5	18.5	28.1	実施例
4- 5	20	0.8	12.3	17.2	25.3	実施例

hは時間、dは日、カルシウムアルミネートはセメント100重量部に対する重量部、圧縮強度の-は強度不足で採取不能。

Table 4

Exprimtent	Calcium Aluminate	Compression Strength			Notes
					Carried Out Example [Translator's Note: 6Entries]

[Underneath Table 4]

h is hours, d is days, parts by weight of the coagulation promotion agent is against 100 parts by weight of cement. " - " under compression strength was impossible to extract because of lack of pressure.

[0054]

(Working Example 5 )

Mixing cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight, it made spraying concrete, 10 parts by weight mixing the quick setding agent which mixes coagulation



promotion medicine of quantity which is shown in calcium aluminate 100 parts by weight and Table 5 in relation to cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, followed compressive strength with specified material age to method of Working Example 4 and measured.

Result is shown in Table 5.

[0055]

[Table 5]

実験 No.	凝結促進 剤	圧縮強度(N/mm <sup>2</sup> )				備考
		3h	1d	7d	28d	
3-6	0	0.5	10.8	18.4	31.2	実施例
5-1	A 0.5	0.6	10.9	18.6	31.5	実施例
5-2	A 1	0.8	11.2	18.6	31.5	実施例
5-3	A 5	1.0	11.3	18.8	31.3	実施例
5-4	A 10	1.2	11.4	19.0	31.2	実施例
5-5	A 30	1.2	11.5	18.7	31.0	実施例
5-6	A 50	1.3	11.6	18.0	29.3	実施例
5-7	B 0.5	0.6	10.9	18.5	31.8	実施例
5-8	B 1	0.7	11.4	18.9	31.7	実施例
5-9	B 5	0.9	11.6	19.1	31.5	実施例
5-10	B 10	1.0	11.5	18.9	31.5	実施例
5-11	B 30	1.3	11.7	19.0	30.2	実施例
5-12	B 50	1.3	11.4	18.3	29.6	実施例
5-13	C 10	0.9	11.2	18.6	31.9	実施例
5-14	A10, B10	1.2	12.0	19.4	32.0	実施例
5-15	A10, C10	1.2	12.1	19.6	31.9	実施例
5-16	B10, C10	1.1	11.8	19.5	31.6	実施例
5-17	* 20	1.2	12.0	19.6	32.0	実施例

\*はA : B : C = 4 : 3 : 3の重量比で混合した混合物、hは時間、dは日、凝結促進剤はカルシウムアルミネート100重量部に対する重量部。

Table 5

Experiment	Coagulation watering agent	Compression Strength		Notes	
					Carried Out Example [Translator's Note: 18 Entries]

[Underneath Table 5]

\*is a mixed compound with relative parts by weight A:B:C = 4:3:3

h is hours, d is days, and parts by weight of the coagulation promotion agent is against 100 parts by weight of calcium aluminate.

[0056]

(Working Example 6)

Mixing cement 100 parts by weight and high performance de-watering agent 10.3 parts by weight, it made spraying concrete, quick setting agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A 10 parts by weight, mixing the quantity which shows in Table 6, in relation to cement 100 parts by weight it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, followed compressive strength to method of Working Example 4 and measured.

Result is shown in Table 6.

[0057]

[Table 6]

実験 No.	凝結 促進 剤	急 結 剤	圧縮強度(N/mm <sup>2</sup> )				備考
			3h	1d	7d	28d	
4-1	-	0	0	-	17.2	38.5	比較例
6-1	A	1	0.2	-	17.0	37.0	実施例
6-2	A	5	0.6	9.9	17.8	35.4	実施例
5-4	A	10	1.2	11.4	19.0	31.2	実施例
6-3	A	15	1.6	12.9	20.1	27.1	実施例
6-4	A	20	2.1	13.4	20.2	24.4	実施例
6-5	B	1	0.1	-	17.1	37.2	実施例
6-6	B	5	0.5	10.1	18.0	35.8	実施例
5-10	B	10	1.0	11.5	18.9	31.5	実施例
6-7	B	15	1.4	12.1	19.6	28.3	実施例
6-8	B	20	1.8	12.8	20.0	24.8	実施例
6-9	C	10	0.9	11.2	18.6	31.9	実施例
6-10	*	10	0.7	11.5	19.3	31.3	実施例

\*はA : B : C = 4 : 3 : 3の重量比で混合した混合物、hは時間、dは日、急結剤はセメント100重量部に対する重量部、圧縮強度の-は強度不足で採取不能。

Exprimment	Coagulation promotion agent	Setding agent			Compression Strength		Notes
							Compression Example
							Carried Out Example [Translator's Note: 12 Entries]

[Underneath Table 6]

\*is a mixed compound with relative parts by weight A:B:C = 4:3:3

h is hours, d is days, and parts by weight of the setding agent is against 100 parts by weight of cement. . " - " under compression strength was impossible to extract because of lack of pressure.

[0058]

(Working Example 7)

It made unit amount of each material similar to Working Example 1, used coarse aggregate and fine aggregate of chart dry state, mixed cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight and manufactured dry concrete, carried to spraying machine with belt conveyor.

On one hand, 10 parts by weight, were added to dry concrete on belt conveyor quick setting agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight in relation to cement 100 parts by weight.

dry concrete which adds quick setting agent pneumatic transport was done from spraying machine, water way 50 parts by weight ago, in relation to cement 100 parts by weight to execute dry type spraying operation in addition, following compressive strength to method of Working Example 4, was measured due to Y letter tube.

As a result, spraying operation is executed was possible without either plugging or other trouble of pipe.

As for compressive strength of age 3 hours of that time as for compressive strength of  $1.3 \text{ N/mm}^2$  28 days they were  $33.4 \text{ N/mm}^2$

[0059]

Powder amount of dust of this time of also, when it compares with the case where high performance de-watering agent 1 is not added, among when high performance de-watering agent 1 is added in relation to being  $29.6 \text{ mg/m}^3$  with  $19.6 \text{ mg/m}^3$ , method which adds high performance de-watering agent 1 clearly powder dust generated amount was less.

[0060]

(Working Example 8)

Mixing coagulation lag medicine of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10. 3 parts by weight, and Table 7, it made spraying concrete, quick setting agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, followed compressive strength to method of Working Example 4 and measured.

Result is shown in Table 7.

(used material)

coagulation lag medicine  $\alpha$  : marketing citric acid

coagulation lag medicine  $\beta$  : commercial potassium carbonate

coagulation lag medicine  $\gamma$  : commercial citric acid 3 and blend of potassium carbonate 7 (weight ratio )

coagulation lag medicine  $\delta$  : marketing ethyleneglycol

coagulation lag medicine  $\epsilon$  : marketing sodium tripoly phosphate

coagulation lag medicine  $\zeta$  : marketing sodium borate

[0061]  
[Table 7]

実験 No.	凝結遅 延剤	圧縮強度(N/mm <sup>2</sup> )			備考
		3h	1d	28d	
5-4	0	1.2	11.4	31.2	実施例
8-1	$\alpha$ 0.05	1.1	11.3	31.1	実施例
8-2	$\alpha$ 0.1	0.9	11.3	31.2	実施例
8-3	$\alpha$ 1.0	0.6	10.5	30.2	実施例
8-4	$\alpha$ 2.0	0.4	10.0	30.0	実施例
8-5	$\alpha$ 3.0	0.2	9.8	28.2	実施例
8-6	$\beta$ 0.1	1.2	11.2	31.0	実施例
8-7	$\beta$ 0.5	1.4	11.1	31.0	実施例
8-8	$\beta$ 1.0	1.6	11.0	30.6	実施例
8-9	$\beta$ 5.0	1.3	10.5	30.3	実施例
8-10	$\beta$ 10.0	0.9	10.1	29.7	実施例
8-11	$\gamma$ 0.1	1.2	11.8	31.8	実施例
8-12	$\gamma$ 0.5	1.0	11.7	31.6	実施例
8-13	$\gamma$ 1.0	0.9	11.5	31.5	実施例
8-14	$\gamma$ 5.0	0.7	10.2	30.1	実施例
8-15	$\gamma$ 10.0	0.5	9.5	28.6	実施例
8-16	$\delta$ 0.1	1.2	11.3	31.0	実施例
8-17	$\delta$ 0.5	0.8	10.8	30.5	実施例
8-18	$\delta$ 1.0	0.7	10.0	30.1	実施例
8-19	$\delta$ 3.0	0.4	9.6	28.7	実施例
8-20	$\delta$ 5.0	0.2	9.0	27.2	実施例
8-21	$\epsilon$ 0.1	1.1	10.9	31.0	実施例
8-22	$\epsilon$ 0.2	0.9	10.4	30.3	実施例
8-23	$\epsilon$ 1.0	0.7	10.1	30.0	実施例
8-24	$\epsilon$ 2.0	0.5	9.5	27.4	実施例
8-25	$\epsilon$ 5.0	0.2	9.0	25.2	実施例
8-26	$\zeta$ 0.1	1.1	11.0	31.2	実施例
8-27	$\zeta$ 0.5	1.0	10.7	30.9	実施例
8-28	$\zeta$ 1.0	0.9	10.4	30.1	実施例
8-29	$\zeta$ 5.0	0.7	9.7	29.6	実施例
8-30	$\zeta$ 10.0	0.4	8.9	28.2	実施例

凝結遅延剤はセメント100重量部に対す  
る重量部。

Table 7

Exprimpt	Coagulation Slowing agent	Compression Strength		Notes	
					Carried Out Example [Translator's Note: 31 Entries]

[Underneath Table 7]

Parts by weight of the coagulation slowing agent is against 100 parts by weight of cement.

[0062]

(Working Example 9)

Mixing powder dust decreasing agent of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10.3 parts by weight, and Table 8, it made spraying concrete, quick setting agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A 10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, measured powder amount of dust and rebound ratio.

Result is shown in Table 8.

(used material)

Powder dust decreasing agent A : marketing methyl cellulose

Powder dust decreasing agent E : marketing hydroxypropyl cellulose

[0063]

[Table 8]

実験 No.	粉塵低減 剤	粉塵量 ( $\text{mg}/\text{m}^3$ )	リバウ ン率 (%)	備考
5-4	0	23.5	22.3	実施例
9-1	A 0.001	20.1	19.2	実施例
9-2	A 0.01	10.4	17.1	実施例
9-3	A 0.05	5.2	10.6	実施例
9-4	A 0.1	2.9	9.5	実施例
9-5	A 0.3	1.7	8.6	実施例
9-6	A 0.5	1.0	7.0	実施例
9-7	A 1.0	0.4	4.2	実施例
9-8	E 0.3	2.1	10.0	実施例

粉塵低減剤はセメント100重量部に対  
する重量部。

Table 8

Exprimtent	Dust decreasing agent	Amount of dust	Rebound rate	Notes
				Carried Out Example [Translator's Note: 9 Entries

[Underneath Table 8]

Parts by weight of the powder decreasing agent is against 100 parts by weight of cement.

[0064]

(Working Example 10)

Mixing ultra fine powder of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10.3 parts by weight, and the Table 9, it made spraying concrete, quick setting agent which mixes the calcium aluminate 100 parts by weight and coagulation promotion medicine A 10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, measured rebound ratio.

Result is shown in Table 9.

(used material)

ultra fine powder a: commercial fumed silica, average particle diameter 10  $\mu$ m or less

ground product, average particle diameter 10  $\mu$ m or less of ultra fine powder b: commercial furnace slag

[0065]

[Table 9]

実験 No.	超微粉	リバ ン 率 (%)	備考
5-4	0	22.3	実施例
10-1	a 1	19.0	実施例
10-2	a 2	18.0	実施例
10-3	a 5	17.7	実施例
10-4	a 10	13.6	実施例
10-5	a 30	11.5	実施例
10-6	a 50	8.7	実施例
10-7	a 100	7.4	実施例
10-8	b 1	21.0	実施例
10-9	b 2	19.7	実施例
10-10	b 5	19.0	実施例
10-11	b 10	15.2	実施例
10-12	b 30	13.0	実施例
10-13	b 50	9.0	実施例
10-14	b 100	8.2	実施例

超微粉はセメント100重量部  
に対する重量部。

Table 9

Experiment	Ultra fine powder	Rebound rate	Notes
			Carried Out Example [Translator's Note: 15 Entries

[Underneath Table 9]

Parts by weight of the Ultra fine powder is against 100 parts by weight of cement.

[0066]

(Working Example 11)

Mixing fiber of quantity which is shown in cement 100 parts by weight, high performance de-watering agent 10.3 parts by weight, and the Table 10, it made spraying concrete, quick setting agent which mixes the calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, 10 parts by weight mixing in relation to the cement 100 parts by weight, it executed other than thing which it makes quick setting characteristic spraying concrete, in same way as Working Example 3, measured impact resistance.

Result is shown in Table 10.

(used material )

fiber i: commercial vinylon fiber, fiber length 10 mm

fiber ii: commercial steel fiber, fiber length 30 mm

(measurement method )

You placed on standard sand which trains those which cut off the spraying concrete after impact resistance: age 3 hours in width 20 cm X length 20 cm X thickness 2.5 cm, to planar sphere of the weight 100g fell from height of 50 cm.

Those which drop times destroys within 5 times were designated as the X, without destroying ○, without destroying those where crack enters those where crack does not enter were done ◎ with.



[0067]

[Table 10]

実験 No.	繊維	耐衝 撃性	備考
5- 4	i 0.0	×	実施例
11- 1	i 0.5	○	実施例
11- 2	i 1.0	◎	実施例
11- 3	i 3.0	◎	実施例
11- 4	i 5.0	◎	実施例
11- 5	i 7.0	○	実施例
11- 6	ii 3.0	◎	実施例

繊維はセメント100重量部に  
対する重量部。

Table 10

Exprimment	Fiber	Impact resistance	Notes
			Carried Out Example [Translator's Note: 7 Entries

[Underneath Table 9]

Parts by weight of the fiber is against 100 parts by weight of cement.

[0068]

(Working Example 12 )

It made quantity which shows unit amount of cement in Table 11, it made quantity which shows amount used of water in Table 11 in relation to cement 100 parts by weight, mixed cement 100 parts by weight and high performance de-watering agent 10. 3 parts by weight and made spraying concrete, quick setding agent which mixes calcium aluminate 100 parts by weight and coagulation promotion medicine A10 parts by weight, mixing 10 parts by weight in relation to cement 100 parts by weight, it executed other than the thing which it makes quick setding characteristic spraying concrete, in the same way as Working Example 3.

Concerning spraying concrete, slump immediately after mixing was measured.

Result is shown in Table 11.

[0069]

[Table 11]

実験 No.	セメ ント	水	スランプ (cm)	圧縮強度(N/mm <sup>2</sup> )			備 考
				1h	1d	28d	
12-1	550	35	8.0	3.2	19.9	47.0	実施例
12-2	500	40	13.5	2.6	17.0	41.7	実施例
12-3	450	45	16.0	2.0	14.4	38.3	実施例
12-4	400	50	17.0	1.5	12.5	33.8	実施例
12-5	400	55	20.0	1.2	10.8	31.7	実施例
12-6	380	60	24.0	0.8	9.2	28.8	実施例

hは時間、dは日、セメント量はkg/m<sup>3</sup>、水はセメント100重量部に対する重量部。

Table 11

Exprimtent	Cement	Water	Slump			Compression Strength		Notes
								Carried Out Example [Translator's Note: 6 Entries]

[Underneath Table 11]

h is hours, d is days, cement amount is kg/m<sup>3</sup>. Parts by weight of water is against 100 parts by weight of cement.

[0070]

#### [Effects of the Invention]

Is kneaded spraying concrete with such as trouble of spraying machine and by using the spraying material of this invention, necessity to leave occurring, spraying concrete and quick setting characteristic spraying concrete to which flow property is large over lengthy, is superior in strength manifestation, powder dust decrease, and rebound decrease are acquired.

spraying material of also, this invention because it is a powder, as cement and various cement filler premix be able to designate, be able to improve the workability beforehand, from high quality spraying material can be adjusted.

Furthermore, jointly using with cellulose type powder dust decreasing agent, be able to maintain de-watering effect and dispersing effect, it can hold down also the obstruction of strength manifestation characteristic.